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Enhanced Adhesion of EVA Laminates to Primed Glass Substrates Subjected to Damp Heat Exposure

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ENHANCED ADHESION OF EVA LAMINATES TO PRIMED GLASS SUBSTRATES SUBJECTED TO DAMP HEAT EXPOSURE

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ABSTRACT

We investigated the effectiveness of glass-surface priming to promote enhanced adhesion of EVA laminates during damp-heat exposure at 85°C and 85% relative humidity. The primary objective was to develop advanced encapsulant formulations by incorporation of various primer formulations that exhibit improved adhesion during damp-heat exposure. Several primer formulations were identified that greatly enhanced the EVA adhesion strength, including to the extent that peeling could not be initiated, even for the laminates of the glass substrate/fast-cure EVA15295P/TPE backsheet (a Tedlar/ polyester/EVA tri-laminate) that were exposed in a damp-heat test chamber for more than 750 h. The results show that a synergistic increase in the interfacial hydrophobicity, siloxane density, and cross-linking density are the key attributes to the improvement in the EVA adhesion strength.

INTRODUCTION

A critical issue in the long-term performance and reliability of PV modules [1], especially polycrystalline thin-film modules [2] without frames and edge seals, is their resistance to moisture ingress. Passing the stringent damp-heat test at 85°C and 85% relative humidity (RH) for 1000 h in the IEEE 1262 qualification test has proven difficult for many thin-film modules; delaminations of thin-film solar cells, encapsulants, and/or backsheets have occurred. Five workshops have been held in the last few years to discuss and address the related moisture ingress and thin-film reliability issues [3-7]. Moisture vapor is well known to cause multiple problems on polymers as well as adhesive joints. Upon absorption of water, a polymer may become swollen, plasticized, and/or hydrolyzed if its component bonding is susceptible to hydrolysis (such as the ester linkage in polyester at high pH). Generally, water can decrease the glass transition temperature, tensile strength, and modulus of a polymer, but increase its elongation at break. These properties can recover fully when the polymer is dried, unless irreversible hydrolysis has occurred. The deterioration of a polymer is greater and faster in higher relative humidity and temperature than in liquid water, because permeation of the vapor is more rapid [7]. The moisture ingress properties of a polymer can be assessed by its permeability coefficient (P) and the diffusion constant (D) of water [8,9]. For example, values of P for more water-resistant polyisobutylene (PIB), phenolic, and epoxy polymers at 25°C are 7-22, 166, and 10-40 x 10^{-9} (cm^3 (STP) cm)/(cm^2 s cm Hg), respectively. For less water-resistant polyvinyl acetate at 40°C, P is 600 x 10^{-9} (cm^3 (STP) cm)/(cm^2 s cm Hg). The corresponding D values for the last three polymers (N/A for PIB) are 0.2-10, 2-8, and 150 x 10^{-9} m^2/s, respectively [8]. For structural polymeric adhesives, moisture ingress is seldom the dominant factor that affects durability. A more important issue is how the moisture influences the adhesive–adherend interface region because of possible preferential accumulation of moisture at the joint interface resulting in loss of adhesion [9,10].

Among a number of encapsulant materials for photovoltaic modules, ethylene-vinyl acetate (EVA) copolymer has been the one most commonly used since the mid-1980s. The commercial products of EVA have been found to fairly easily delaminate from glass substrates upon prolonged immersion in an 85°C water bath [11] or exposure to damp-heat, as observed in our laboratories. To improve the adhesion strength of adhesives against moisture-induced degradation, surface priming and use of alternative non-EVA adhesives, along with adequate substrate cleaning to reduce the surface contamination, are among a number of approaches that can be taken [11,12]. For example, Tucker investigated adhesion of two non-EVA polymers (CPVC and PMMA) on glass and compared the effectiveness of two silanes in enhancing EVA's long-term adhesion durability against damp-heat exposure, but with limited success [13]. The key concepts in formulating the primer solutions in this work were to use mixed silanes to introduce higher degrees of (1) surface hydrophobicity to exclude water molecules from the interfacial regions, (2) siloxane bonding density at the glass/EVA interface, and/or (3) cross-linking extent between the interfacial silanes and the EVA. Custom-formulated EVA and non-EVA polymers were also studied.

EXPERIMENTAL

The primer formulations consisted of various combinations of silane-based coupling agents at a 2%

total volumetric concentration in pH=5.0, 95:5 (v/v) ethanol/H_2O mixture [14]. Table 1 shows the types of silane coupling agents and their interfacial functionality or purposes being studied. Table 2 lists the silane combinations of primer formulations used for the samples, but the exact concentration ratios of several were not indicated for proprietary reasons. Commercial low-iron, soda lime glass plates, AFG Krystal Klear®, 3.2 mm (1/8") thick at a size of 10 cm x 10 cm (4" x 4"), were used. To ensure good silanization, the glass plates were thoroughly cleaned by first cleaning with diluted Liqui-Nox® for 15 min in a ultrasonicator, followed by soaking for about 30 min each in 1:1 (v/v) methanol/HCl and then in concentrated H_2SO_4; this was followed by rinsing with copious deionized H_2O between and after acid soaking [15]. The cleaned glass surface gave an average contact angle of ~4.5° for water droplets (versus ~52.2° for the plates cleaned by the IPA-then-Billco 79A® scrubbing method used by some PV manufacturers). Priming was conducted by immersing the glass plates in the primer solutions for 2 min followed by brief rinsing with ethanol. The primed glass plates were then treated at ~93°–97°C in a preheated oven for 10–12 min. A commercial fast-cure EVA15295P/UF (0.46 mm thick), manufactured by Specialized Technology Resources (STR), was used for most sample laminations to the non-tinned glass surface side. Some custom-formulated, self-primed EVA and PMG formulations were also included in the test matrix. The PMG was an ethylene copolymer of methylacrylate containing glycidyl methacrylate. A total of 32 laminates were prepared with a common configuration of TPE/encapsulant/glass. The gel contents of the fast-cured EVA-15295, custom-formulated EVA, and PMG were analyzed using tetrahydrofuran extraction to be 90%-92%, 84%-86%, and 52%-64%, respectively. Damp-heat exposures were conducted in a Blue M, Model AC-7602HB chamber. The adhesion strength of the candidate encapsulants to the glass substrate was measured periodically using an Instron Model 5500 system with a 90-degree pull [16] and a cross-head speed of 10 mm/min. Typically, a 4-h dry-out was allowed before the peel tests were conducted.

Table 1. Silanes and their Interfacial Application Purposes

Silane ID/Functional Group	Interfacial Functionality or Purpose
Z-6030®, Methacrylate-	Cross-linking
Z-6032®, Vinylbenzyl-	Cross-linking and hydrophobicity
Vinyl-, Epoxy-	Cross-linking and hydrophobicity
Dipodal, Polysiloxane	Cross-linking and siloxane-concentration enhancing
Amino-, Diamino-	Cross-linking and catalytic; but can be hydrophilic
Fluoro-, Isobutyl, Phenyl-	Hydrophobicity

Table 2. Ranking Order of Primer Formulations and Self-Primed Encapsulants based on Time-Averaged Peel Strength as a Function of Damp-Heat Exposure

Sample ID	Base Silane	Silane #2	Silane #3	Init. PS (N/mm)	TAPS[1] (N/mm)	ΔPS[2] (N/mm)	Rank Order
PMG-K, D6-1[3]	Z-6030	Epoxy-	(Self-Primed[4])	9.50	9.62	2.86	1
Z6030-J[3]	Z-6030	Fluoro-	Dipodal	9.75	9.56	2.79	2
Z6030-C	Z-6030	Vinyl-	N/A	10.25	9.32	2.56	3
Z6032-B[3]	Z-6032	Dipodal	Amino-	9.00	9.27	2.51	4
Z6032-A[3]	Z-6032	Vinyl-	Amino-	11.50	9.15	2.39	5
Z6030-E	Z-6030	Fluoro-	N/A	9.50	8.83	2.07	7
Z6030-L	Z-6030	Phenyl-	N/A	11.00	8.72	1.96	8
Z6030-M	Z-6030	Phenyl-	Diamino-	11.00	8.69	1.93	9
Z6030-G	Z-6030	Fluoro-	Amino-	10.50	8.66	1.90	10
Z6030-I[3]	Z-6030	Epoxy-	Amino-	10.50	8.40	1.64	13
Z6030-D	Z-6030	Dipodal	N/A	10.00	8.38	1.62	15
Z6030-K	Z-6030	Diamino-	N/A	11.00	8.21	1.45	16
Z6032-C	Z-6032	Vinyl-	Diamino-	10.00	7.83	1.07	18
Z6030-S	Z-6030	Phenyl-	Dipodal	11.00	7.59	0.83	19
Z6030-A	Z-6030	N/A	N/A	9.50	7.58	0.82	20
Z6030-B	Z-6030	Amino-	N/A	11.50	6.93	0.17	24
EVA-B, F/E-2	Z-6030	Polysiloxane	(Self-Primed[4])	10.25	6.93	0.17	25
Control	Z-6030		(Self-Primed[4])	6.76	6.76	0.00	26

[1] Time-averaged peel strength after 500-h damp-heat test.
[2] Difference in time-averaged peel strength from the control sample after 500-h damp-heat test.
[3] Peeling could not be initiated because of TPE failure at T0 and subsequent damp-heat test intervals.
[4] The "self-primed" indicates the silane(s) was/were already blended in the extruded films. No glass priming for the sample.

RESULTS AND DISCUSSION

In the commercial "self-primed" EVA formulations [13], a functional silane coupling agent such as Z6030® (Dow Corning) is commonly used to enhance EVA adhesion strength to glass substrates by forming Si-O-Si siloxane bonds with the hydroxyl groups on the glass surface via a condensation reaction. Without the silane,

the EVA adhesion strength would be about six to ten times weaker [11,13]. However, in the presence of moisture and elevated temperatures, the Si-O-Si bonding is reversible by hydrolysis. A possible solution to the problem is to reduce the "free space" at the interfacial regions to exclude water molecules from accumulating at the interfacial regions. This was achieved by using silanes such as fluoro-, dipodal, phenyl-, and vinyl- (Table 1) for a greater degree of hydrophobicity and density of siloxane bonding between the silane and glass in formulating the primer solutions. To increase the cross-linking between the silane and EVA, functional silanes such as methacrylate (Z-6030), vinylbenzyl (Z-6032), and vinyl were used. Amino silanes were used primarily as catalysts. Similar approaches of using mixed silanes for various polymer materials are reported in the literature [17-20].

Figure 1 compares the peel strength (PS) data for six samples laminated with the glass substrates primed with Z-6030-based primer solutions with a unprimed-glass "control" as a function of damp heat exposure time to 500 h. Figure 2 shows the peel strength plot for three samples laminated with the glass substrates primed with Z-6032-based primer solutions, one custom-formulated EVA-B, and two PMG-K samples. Upon longer exposures to ~750–775 h, the TPE film was largely weakened or degraded, with interlayer delamination of Tedlar/PET (TP) from EVA (E). This delamination prevented reliable peel strength measurements from being made and shown in both figures. As seen in Fig. 1, all the samples with Z-6030-based primed glass substrates exhibit higher initial peel strength than that of the control with unprimed-glass substrate. Their resistance to damp-heat exposure is also generally better than the control, although two showed a worse trend at 500 h. Similar results are observed in Fig. 2 for samples with Z-6032-base primed glass substrates. For the EVA-B that was custom-formulated with Z-6030 and a H-terminated polysiloxane (H-PDMS) and laminated to the unprimed-glass substrate, a high initial peel strength was followed by rapid deterioration of adhesion strength after being exposed to damp heat. However, in a separate study, the H-PDMS catalytically primed on glass substrates had shown very good resistance to hydrolytic

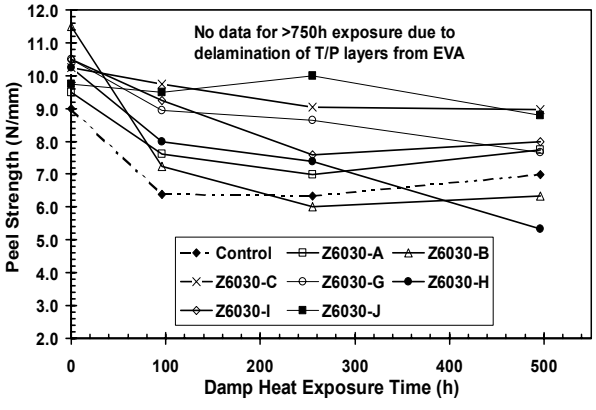

Fig. 1. Peel strength measured for eight TPE/EVA/ glass laminates exposed to damp heat for ~500 h.

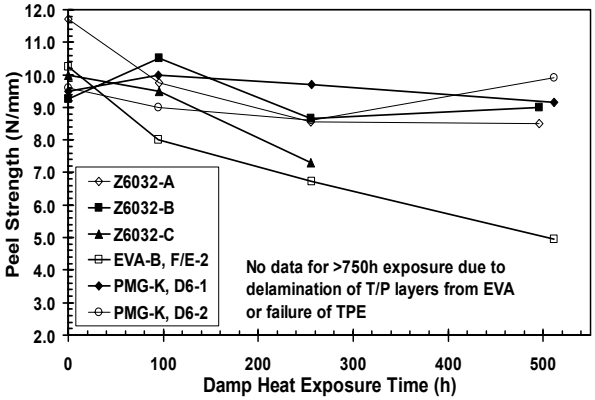

Fig. 2. Peel strength measured for six TPE/EVA (or PMG)/glass laminates exposed to damp heat for 500 h

loss when soaked in an 85°C water bath. The presence of H-PDMS polysiloxane was observed to cause a great degree of difficulty for the EVA-B and PMG-B formulation to be extruded into films. For PMG-K formulated with Z-6030 and a second epoxy-type silane, film extrusion problems were not observed, and the loss of adhesion strength during damp-heat exposure was relatively small, as seen in Fig. 2.

To evaluate and compare the effectiveness of the various primer formulations on enhancing EVA adhesion during damp-heat exposures, a statistical analysis of comparative time-averaged performance (i.e., "TAPS" in Table 2) was employed. A test criterion, *w*, was defined, which depends on the estimated standard deviation of the acquired data and the percentiles of the studentized range, q [21].

$$w = \frac{q_{1-\alpha} \cdot \sigma}{\sqrt{n}}$$

For a confidence interval of 99%, *w* was determined to be *0.94* N/mm for the set of 32 samples. If the difference in TAPS between two samples is greater than *w*, then we conclude with 99% confidence that a primer produced a statistically significant improvement in peel strength between the two samples. The results of calculated TAPS, their difference from the control (ΔPS), and the ranking order are given in Table 2 for 18 of the 32 samples and their (unduplicated) primer silane combinations. The six samples that performed poorer than the control are not shown. A comparison of the ΔPS indicates that primer formulations Z-6030-A, B, S, and EVA-B F/E-2, with ΔPS in the 0.17–0.83 range (< 1 *w,* rank order from 19 to 25), offer statistically insignificant improvements versus the unprimed control. For the other samples that show ΔPS in the 1.07–1.96 range (rank order from 8 to 18), the largest spread, 2.80(Z6030-L) – 1.62(Z6032-C) = 0.89, is less than *w* = 0.94, further suggesting the adhesion strength improvements provided by these primer solutions are statistically comparable. For those primer formulations ranking from 2 to 7 in Table 2 with 2.07 < ΔPS < 2.79, the improvements on the adhesion strength during damp-heat exposure are

statistically more significant. Peeling could not be initiated for the four samples, Z-6030-I and J and Z-6032-A and B, before and after damp-heat exposure because of strong EVA adhesion. The peel strength results thus obtained are less accurate for these four samples. However, three of them, excluding Z6030-I, rank among the top five in TAPS values. For self-primed PMG-K D6-1, which ranks No. 1, peeling tests could not be ever truly performed even after 750 h exposure. The enhanced adhesion is attributed to the presence of functional groups of methacrylate and glycidyl methacrylate in the PMG that provide greater bonding than EVA to the glass surface, in addition to the siloxane bonding from Z-6030 and epoxy silane in the formulation. As evaluated from the silane components of primer formulations for the six highest TAPS, the mechanisms responsible for enhanced EVA adhesion during damp-heat exposure are attributed to (1) an increase in the siloxane bonding density via the smaller silane molecules of cross-linking vinyl or dipodal silanes, (2) a presence of hydrophobic fluorosilane, (3) a dominant use of Z6032 vinylbenzyl silane (with vinyl and hydrophobic benzyl), and/or (4) a presence of low-concentration aminosilane serving as a catalyst. These factors have worked synergistically as designed to increase the interfacial hydrophobicity and cross-linking density with the EVA. These results are consistent with those reported in the literature [17-19]. However, the presence of "additional" Z-6030 on the glass surface by priming with Z6030-A (see Table 2) provided only little improvement. A high concentration of amino silane alone (e.g., 25%) was found adverse to reduce adhesion strength by possibly causing the interfacial regions to become relatively more hydrophilic.

CONCLUSIONS

Several primer formulations of mixed silanes are identified from peel tests to enhance the adhesion strength of EVA/glass laminates during prolonged damp-heat exposure. A synergistic increase in the interfacial hydrophobicity, siloxane density, and cross-linking density by the use of carefully selected silane combinations are the key attributes to the improvement. Specifically, the carefully selected silane combinations that provided the most enhanced EVA adhesion consist of (1) an increase in the siloxane bonding density via the smaller silane molecules of cross-linking vinyl or dipodal silanes, (2) a presence of hydrophobic fluorosilane, (3) a dominant use of vinylbenzyl silane (with vinyl and hydrophobic benzyl), and/or (4) a presence of low-concentration aminosilane serving as a catalyst. Self-primed (non-EVA) PMG appears to be very promising for offering high water-resistant potential. For convenience in practical use, the best-performing primer formulations developed in this work have been formulated into EVA encapsulant films for damp-heat tests to further verify their performance.

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